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ω -TERMINATED ALKANETHIOLATE MONOLAYERS ON SURFACES OF COPPER, SILVER AND
GOLD HAVE SIMILAR WETTABILITIES

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ω -Terminated Alkanethiolate Monolayers on Surfaces of
Copper, Silver and Gold Have Similar Wettabilities.¹

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Abstract

Long-chain alkanethiols ($\text{HS}(\text{CH}_2)_n\text{X}$) adsorb from solution onto the surfaces of freshly evaporated copper, silver and gold films and form oriented monolayers. Both polar and non-polar tail groups (X) can be accommodated in these adsorptions. Adsorption on all three metals generates self-assembled monolayers (SAMs) exhibiting similar wetting properties, and thus, by inference, having related oriented structures. XPS data suggest that the ω -terminated *n*-alkanethiolate monolayers, like those derived from simple alkanethiols, are composed of trans-extended chains having orientations on copper and silver that are closer to the perpendicular to the surface than are those on gold. We have prepared and characterized monolayers ("mixed monolayers") by exposure of all three metals to mixtures of $\text{HS}(\text{CH}_2)_{11}\text{OH}$ and $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$. On all three, the wettability of the interfaces covers the range between the extremes: $\theta_a^{\text{H}_2\text{O}} = -10^\circ$ and -115° . Values of the advancing contact angle of water can be related to their composition by Cassie's expression. The similarity in wettabilities of these surfaces, and the fact that wettability is related to surface composition by a simple linear relationship, both argue that $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{CH}_3$ functional groups behave approximately independently at the monolayer-air (water) interface. Interactions between functional groups, and substantial variations in the structure of the underlying polymethylene region of the SAM are much less important in determining interfacial free energies than are the areas the functional groups occupy at the interface.

Introduction

Long-chain alkanethiols ($\text{HS}(\text{CH}_2)_n\text{CH}_3$) adsorb from solution onto the surfaces of copper, silver, and gold and form densely packed, oriented monolayer films (self-assembled monolayers, SAMs) that are attached to the surface as metal thiolates (RS^-M^+).³⁻²² On gold, alkanethiolate monolayers, derived from alkyl thiols or disulfides, have provided systems used for studies of wetting,⁶⁻¹² adhesion,¹³ protein adsorption^{14,15} and electrochemistry.¹⁵⁻¹⁹ These assemblies offer a high degree of control over the thickness of the monolayer, and accommodate a wide range of polar and non-polar tail groups at the opposite terminus of the polymethylene chain from the thiol group (and thus at the interface between the SAM and the vapor or liquid phase contacting it). To date, the self-assembling system reported to be capable of generating the widest variety of organic interfaces is that based on adsorption of ω -substituted alkanethiols on gold.^{6-12,14,17,19-21} Here we report that the chemistry described for alkyl thiolates on gold can be readily extended to alkyl thiolates on silver, and, with greater experimental difficulty, to copper. We also provide data that suggests that, while the alkanethiolate monolayers on silver and copper have structures that are distinct from (although closely related to) those formed on gold, similar wettabilities are observed for corresponding SAMs on all three metals. We and others have described extensive structural studies of unsubstituted alkanethiolates on gold,^{3,16,22} silver^{3,4} and copper.³ The emphasis in the present paper is on alkanethiolates bearing terminal substituents, especially polar ones. Ulman et al.²³ have

reported that monolayers formed by adsorption of $\text{HS}(\text{CH}_2)_{11}\text{OH}$ on silver and gold have different wettabilities: $\theta_a^{\text{H}_2\text{O}} \sim 20^\circ$ and $< 10^\circ$, respectively. We find the wettability of SAMs on silver and gold derived from hydroxyl-terminated alkanethiols, including those derived $\text{HS}(\text{CH}_2)_{11}\text{OH}$, to be the same, although we have observed higher values of $\theta_a^{\text{H}_2\text{O}}$ on silver whose surface has oxidized.

Many self-assembling systems now exist that can generate low-energy surfaces;^{3-6,24,25} however, the number capable of generating high-energy surfaces, in one assembly step, are few. For example, while *n*-alkanoic acids adsorb onto various metal oxides and form oriented, oleophobic monolayers,²⁵ ω -hydroxy- and ω -amino-alkanoic acids adsorb and form poorly organized films that are not wet by water (probably because they form "looped" structures with polar functionalities in both α - and ω -positions coordinated to the surface). Relatively hydrophilic surfaces ($\theta_a^{\text{H}_2\text{O}} = 30-50^\circ$) have been prepared on silica in a two-step procedure: first, adsorption of an alkyltrichlorosilane having a terminal olefin, ester, or alkyl sulfide group on silica;²⁶⁻²⁸ second, chemical transformation of the non-polar terminal group into a more polar group (carboxylic acid,²⁶ alcohol,^{26,27} sulfone²⁸). This type of system has two disadvantages. First, the monolayers of alkylsiloxanes on silica are probably intrinsically less ordered than SAMs on gold and silver,²⁹ and are unquestionably more difficult to prepare in highly-ordered form; second, the reactions used to convert functionalities present in these SAMs to more polar forms certainly proceed in yields less than 100%.³⁰ Thus, the alkylsiloxane monolayers having polar terminal functionality

are probably disordered both in structure and in composition at their termini.

In contrast, interfaces that are both polar and highly wettable (alcohols,^{6,17,21} carboxylic acids,^{6,10,17,21} phosphocholines,²⁰ amides²¹) have been prepared by adsorption of the corresponding alkanethiols onto gold surfaces. We believed the ability of gold to discriminate between hard and soft³¹ tail groups could be extended to surfaces of copper and silver.³²

In a previous paper,³ we have shown that *n*-alkanethiols adsorb onto copper and silver and form oriented, densely packed monolayers. These SAMs differ in one respect from those formed on gold; XPS and IR spectroscopy indicated that the alkyl chains are oriented closer to the perpendicular to the surface of the metal on copper and silver than on gold (cant angles, relative to the surface normal are 13° (copper and silver) and 28° (gold)). We note that the SAMs studied in that report³ and here exhibited no (or little) surface oxide on silver and gold; the monolayers formed on copper were supported on an interphase that contained oxide even though exposure of the unfunctionalized surface to the atmosphere was minimized.

Results and Discussion

Films of copper, silver, and gold were prepared by evaporation of the metals onto pre-cut slides of Cr-primed Si(100) using a resistively heated tungsten filament or an electron beam. The slides were immersed in 1 mM deoxygenated ethanolic solutions³³ of various ω -terminated alkanethiols for 2-12 h and characterized by

measurement of contact angle and XPS. Some SAMs on copper ($X = \text{CH}_3, \text{CH}=\text{CH}_2$) were prepared from isooctane and exhibited lower hysteresis than corresponding SAMs formed from ethanol. The evaporated films of copper and silver were transferred to solution under a flow of Ar; films of gold was transferred under air. Table I summarizes the advancing and receding contact angles of water and hexadecane on the resulting SAMs.

In general, the wetting behaviors observed on the monolayers prepared on silver and copper are similar to those prepared on gold; the hysteresis in the contact angles of water is generally greater on the copper surfaces. We believe that this increase is probably due to the roughening of the metal-air (or monolayer) interface that occurs during oxidation and subsequent adsorption of the thiol. We note that the range of wettabilities -- for $\theta_a^{\text{H}_2\text{O}} \approx 120^\circ$ to $\theta_a^{\text{H}_2\text{O}} < 15^\circ$ -- demonstrated on copper, silver, and gold cannot be achieved in other self-assembling systems.

The only organic groups that yielded highly hydrophilic surfaces ($\theta_a^{\text{H}_2\text{O}} < 20^\circ$) are those that exposed groups capable of hydrogen-bond donation ($\text{OH}, \text{CO}_2\text{H}, \text{CONH}_2$). Alkanethiols terminating in $X = \text{OH}$ or CO_2H did not always yield SAMs on copper that were as hydrophilic as those formed on gold or silver; for $X = \text{OH}$, SAMs were not wet by water only for long-chain ($n > 16$) adsorbates. Carboxylic acids and alcohols will form monolayers on most (if not all) metal oxides;²⁴ we believe that the films formed on our slightly oxidized copper surfaces probably consist, in part, of "looped"³⁴ and/or "inverted" structures. These overall structures would expose a hydrophobic, disordered interface to the contacting

Table I. Static advancing and receding contact angles of water and hexadecane (HD) on films prepared by adsorption of $\text{HS}(\text{CH}_2)_n\text{X}$ on surfaces of gold, silver and copper

Cmpd #	n	X	Molecular Length ^b	Contact angles (advancing, receding; in degrees) ^a					
				Au		Ag		Cu	
				H ₂ O	HD	H ₂ O	HD	H ₂ O	HD
1	2	(CF ₂) ₅ CF ₃	10	119,106	71,62	121,110	79,60	122,106	81,59
2	11	OCH ₂ CF ₂ CF ₃	17	118,105	71,62	119,111	75,61	119,99	69,44
3	7	CH ₃ ^c	10	112,103	46,35	107,93	45,33	115,98	44,31
4	11	CH ₃ ^c	14	115,104	49,36	113,99	46,35	120,99	46,28
5	17	CH ₃ ^c	20	115,105	48,36	116,103	49,35	120,103	48,32
6	21	CH ₃ ^c	24	117,100	49,38	115,103	49,36	117,102	45,34
7	17	CH=CH ₂ ^c	21	105,100	38,28	108,100	44,34	117,96	31,24
8	11	OCOCF ₃ ^d	16	93,83	60,28	93,77	64,32	100,85	58,30
9	10	CO ₂ CH ₂ CH ₃	16	89,77	45,28	89,71	38,19	93,69	31,-
10	11	Cl	13	89,77	<10,-	89,77	<10,-	95,80	<10,-
11	11	OCH ₃	15	85,72	37,11	84,66	38,20	87,57	32,-
12	11	CN	14	68,61	<10,-	74,65	<10,-	72,52	<10,-
13	16	CN	19	70,62	<10,-	75,63	<10,-	77,49	<10,-
14	21	CN	24	74,62	<10,-	78,60	<10,-	80,50	<10,-
15	11	CONHCH ₃	16	76,64	31,-	82,65	29,-	e	e
16	10	CO ₂ CH ₃	15	74,61	38,25	72,64	35,22	70,49	22,-
17	10	OH	13	<15,-	<10,-	<15,-	<10,-	<15,-	<10,-
18	11	OH	14	<15,-	<10,-	<15,-	<10,-	<15,-	<10,-
19	19	OH	22	<15,-	<10,-	<15,-	<10,-	26,-	<10,-
20	22	OH ^f	25	25,-	<10,-	21,-	<10,-	44,20	<10,-
21	10	CONH ₂	14	<15,-	<10,-	<15,-	<10,-	<15,-	<10,-
22	15	CONH ₂	19	<15,-	<10,-	<15,-	<10,-	17,-	<10,-
23	10	CO ₂ H	14	<15,-	<10,-	<15,-	<10,-	35-50,-	<10,-
24	15	CO ₂ H	19	<15,-	<10,-	<15,-	<10,-	53,25	<10,-
25	21	CO ₂ H	25	<15,-	<10,-	<15,-	<10,-	50,25	<10,-

(Table I Cont'd)

^aHD = hexadecane. A dash indicates a receding contact angles for a contacting liquid that could not be removed from the surface. For these systems, $\theta_r \equiv 0^\circ$.

^bMolecular length is defined as the number of contiguous atoms in the adsorbed molecule comprising the monolayer metal/S(CH₂)_nX. These values are used in Figure 1.

^cThe SAM on copper was formed from isooctane. SAMs prepared on copper from this thiol from ethanol routinely exhibited greater hystereses ($\cos\theta_r - \cos\theta_a$) than SAMs adsorbed from isooctane.

^dPrepared by reaction of entry 18 with 5% trifluoroacetic anhydride/hexanes for 30 s.

^eSAMs on copper were difficult to obtain in high quality. The wetting properties of our best samples were: $\theta_a^{\text{H}_2\text{O}} = 65-75^\circ$, $\theta_r^{\text{H}_2\text{O}} = 36^\circ$, $\theta_a^{\text{HD}} = 17^\circ$, $\theta_r^{\text{HD}} \equiv 0^\circ$.

^fA value of $\theta_a^{\text{H}_2\text{O}} \approx 20^\circ$ has been reported for SAMs on gold derived from HS(CH₂)₂₁OH (Evans, S. D.; Sharma, R.; Ulman, A. Langmuir 1991, 7, 156-161).

liquid (vide infra). Alkanethiols terminating in polar groups adsorbed on silver surfaces that contained an oxide interphase also yielded less hydrophilic surfaces; the contact angles reported here on silver (Table I, Entries 17-25) were only obtained when exposure of the evaporated silver to atmosphere was minimized. The adsorption of some fraction of the tail groups to the oxide surface may explain some of the higher contact angles of water observed by Ulman and co-workers for polar organic surfaces formed on silver.²³ We have been able to reproduce the higher contact angles of water reported by Ulman et al. by allowing the silver to oxidize sufficiently before exposure to an ω -hydroxy-alkanethiol. Reports by Ulman et al.²³ that wettability of monolayers derived by adsorption of $\text{HS}(\text{CH}_2)_{11}\text{OH}$ on gold and silver are different, and computations rationalizing this reported difference require, in our opinion, reanalysis: in our experience, the wettability of hydroxyl-terminated alkanethiolate monolayers on silver and gold are the same.

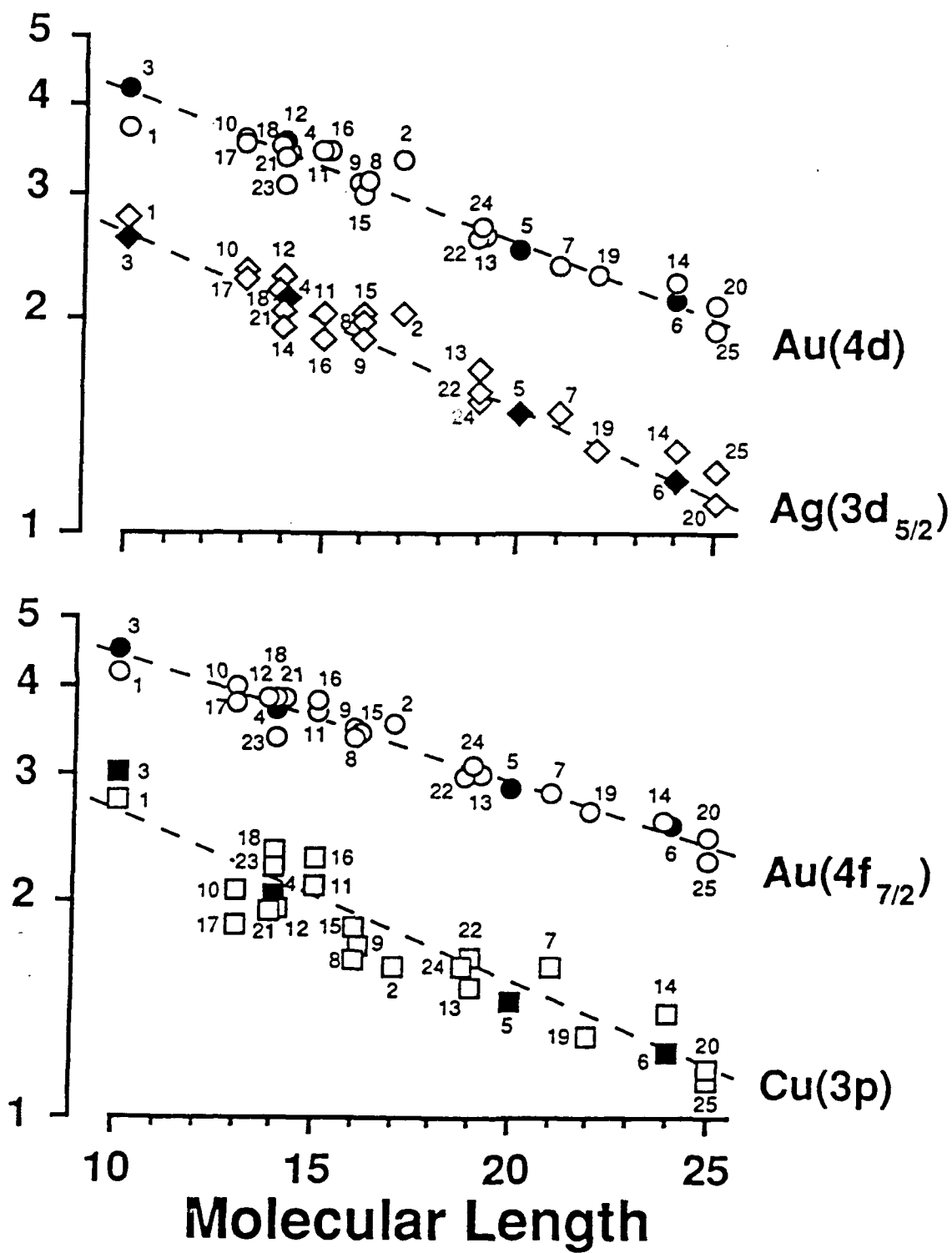
The highly hydrophilic surfaces ($\text{X} = \text{OH}$, CONH_2 and CO_2H ; Entries 17-21) provide an example of the sensitivity of wetting of these systems to structure. Replacement of a hydrogen atom in these structures by a methyl group ($\text{X} = \text{OCH}_3$, CONHCH_3 , CO_2CH_3 ; Entries 11, 15, 16) is sufficient to change these very hydrophilic surfaces to hydrophobic surfaces ($\theta_{\text{a}}^{\text{H}_2\text{O}} \approx 70-90^\circ$) that are also no longer wet by hexadecane; similar effects have been observed previously.^{7,21,35}

The monolayers formed on the three metal surfaces were characterized by XPS to determine their structural similarity to

films formed from simple *n*-alkanethiols (Figure 1); XPS can be used as a measure of the thickness of a film by determining the attenuation of photoelectrons from the underlying substrate by the adsorbed layer.³⁶ We have previously shown for *n*-alkanethiolate monolayers formed on the three metals that conclusions concerning the structure of the SAM drawn from XPS attenuations agreed with those from IR.^{3,37} For this study, the variations in head groups complicate comparison; we adopt the convention of comparing the intensities of photoelectrons due to the substrate to the number of atoms that extend from the sulfur to the end of the tail group in the adsorbed molecule (see Table I). While this treatment is qualitative and does not take full account of differences in the structures of the various tail groups, it provides a useful comparison. The degree of attenuation is also a function of the kinetic energy of the photoelectrons,³⁸ and we compare peaks of similar energies -- that is, in Figure 1, Au(4d) (BE = 1143 eV) with Ag(3d_{5/2}) (BE = 1119 eV); Au(4f_{7/2}) (BE = 1402 eV) with Cu(3p) (BE = 1410 eV). Each datum was obtained in ~3 min and the damage to the monolayers in this interval due to exposure to X-rays was negligible. Figure 1 shows that the attenuation, and thus the relative thicknesses of the monolayers containing tail groups of differing polarity but commensurate in size with the polymethylene chains, are similar to those derived from *n*-alkanethiols throughout a series on a particular metal. We stress that the XPS data presented here imply that *the functional groups are supported on a hydrocarbon layer ((CH₂)_n) that is analogous in thickness and thus in packing density to simple n-alkanethiolate monolayers on*

Figure 1. Intensity of photoelectrons due to the underlying metal substrate for various monolayers adsorbed on the surfaces of copper (\square), silver (\diamond), and gold (\circ) from absolute ethanol. We define "molecular length" as the number of contiguous atoms in the adsorbate spanning the monolayer. (For example, for metal/ $\text{SCH}_2\text{CO}_2\text{CH}_3$ the molecular length would be 6.) The numeric labels refer to compounds listed in Table I. Absolute photoelectron intensities are a function of instrumental parameters and the sets of data have been offset vertically to facilitate comparison; only the slopes are important here. The kinetic energies of photoelectrons for each graph are similar: $\text{Au}(4f_{7/2}) = 1402 \text{ eV}$ and $\text{Cu}(3p) = 1412 \text{ eV}$; $\text{Au}(4d) = 1143 \text{ eV}$ and $\text{Ag}(3d_{5/2}) = 1119 \text{ eV}$. The filled symbols correspond to SAMs derived from *n*-alkanethiols ($\text{X} = \text{CH}_3$). Dashed lines were determined from linear least square fits to data obtained from adsorption of *n*-alkanethiols on the three metals; the higher slopes obtained on copper and silver demonstrate that the SAMs formed on these metals are oriented closer to the surface normal than those formed on gold: $\text{Au}(4d) = -0.049$ vs. $\text{Ag}(3d_{5/2}) = -0.057$; $\text{Au}(4f_{7/2}) = -0.041$ vs. $\text{Cu}(3p) = -0.051$.

XPS Intensity (Arbitrary units)



the various metals.³⁹ These differences in the change in thickness with atomic length between SAMs formed on the three metals suggest that the orientation of the axis of the polymethylene chain is closer to the normal to the surface on copper and silver than on gold. The XPS data do not, however, indicate anything about fine details of structure, especially the orientation of the tail groups. At room temperature, calculations by Hautman and Klein indicate the tail groups to be dynamic and disordered.^{40,41}

The XPS attenuation of the films formed on copper by exposure to $\text{HS}(\text{CH}_2)_n\text{CO}_2\text{H}$ or $\text{HS}(\text{CH}_2)_{19,22}\text{OH}$ suggests that the packing density of the film approximates a densely packed oriented monolayer. The wettabilities of these films are, however, inconsistent with the formation of an interface comprising densely packed carboxylic acid or hydroxyl groups (vide supra). The films were examined further by XPS. High resolution spectra of the S(2p) region revealed a broad envelope that could not be fit by a single spin-orbital doublet. The presence of intensity at slightly higher binding energies ($\Delta = 1$ eV) from that expected for metal-thiolates suggests that some of the sulfur-containing species are present as thiols. Similar wetting and XPS features could be observed on silver that had been highly oxidized.

Mixed Monolayers Adsorbed from Ethanol Solution. In a further comparison of the characteristics of SAMs on the three metals, we determined contact angles on mixed monolayers^{8,9} prepared by adsorbing $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{11}\text{OH}$ from 1 mM ethanolic solutions containing mixtures of these two compounds. The metals were exposed to the contacting solution for 2 h. The

wettabilities of the resulting monolayers for various compositions of the solutions and of the resulting SAMs are plotted in Figure 2. The surface compositions were determined from XPS by comparing the intensity of the O(1s) peak in the mixed monolayer to the intensity of the monolayer derived from pure HS(CH₂)₁₁OH.

Determinations of the surface compositions on copper were complicated by the presence of surface oxide and are therefore slightly less accurate than on gold and silver.⁴² The three systems were dynamic: the films incorporated more dodecanethiol and became increasing hydrophobic with extended exposure to the ethanolic solutions. The relation between wettability and surface composition did not change with time and we have included data from longer exposure times in the lower panel of Figure 2.

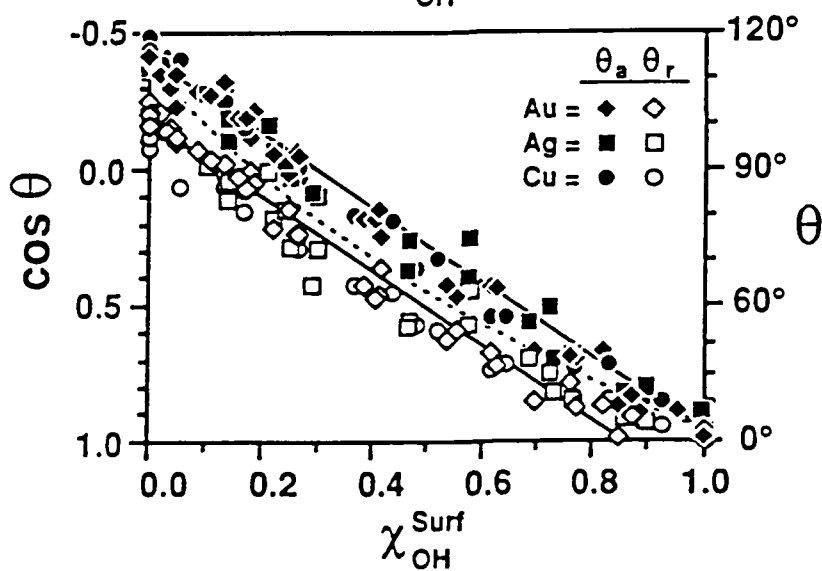
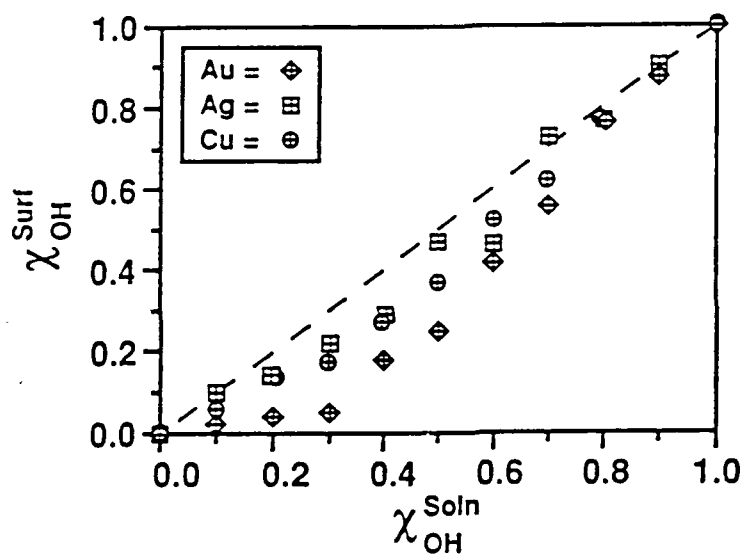
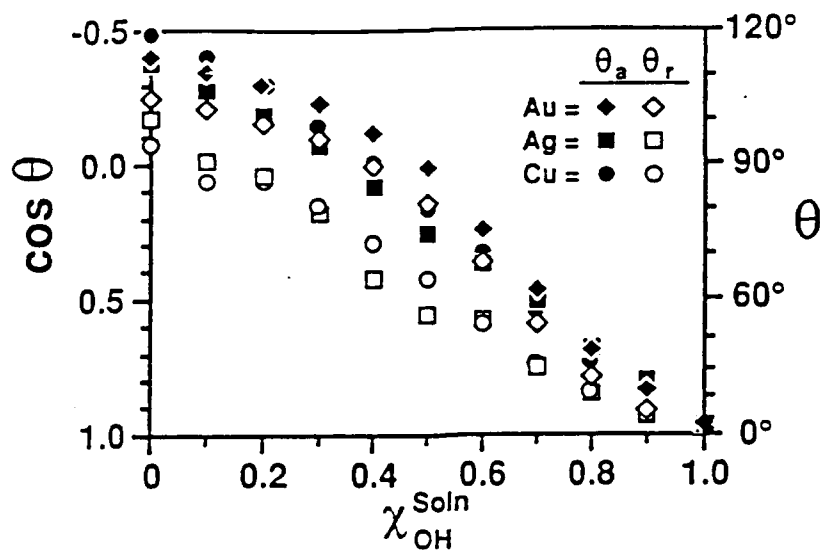
On all three metals, the SAMs exhibited similar wettabilities at the same value of the mole fraction of the hydroxyl-containing component in solution (χ_{OH}^{Soln}) or on the surface (χ_{OH}^{Surf}). The two alkanethiols adsorb on the three metals forming monolayers of similar compositions, and the wettability of these mixed monolayers is better described by Cassie's equation⁴³ (eq 1), than by eq 2 suggested by Israelachvili and Gee⁴⁴ (Figure 2).

$$\cos\theta = f_1\cos\theta_1 + f_2\cos\theta_2 \quad (1)$$

$$(1 + \cos\theta)^2 = f_1(1 + \cos\theta_1)^2 + f_2(1 + \cos\theta_2)^2 \quad (2)$$

In eq 1 and 2, f_n is defined as the fractional area of the surface that is type n , and θ_n as the contact angle on a pure homogeneous surface of type n ; hydroxyl and methyl groups are sufficiently similar in size that we assume f_n and χ_n^{Surf} are equivalent for the

Figure 2. Comparison of monolayers adsorbed on copper (○), silver (□), and gold (◇) from mixtures of $\text{HS}(\text{CH}_2)_{11}\text{OH}$ and $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ dissolved in ethanol after 2 h exposure. Solutions were 1 mM in total thiol concentration. Advancing and receding contact angles (filled and open symbols, respectively) were measured on static drops of water. Surface compositions (patterned symbols) were determined from XPS by scaling the O(1s) signal to that obtained on the pure $\text{HS}(\text{CH}_2)_{11}\text{OH}$ -derived monolayer; the background level of oxygen on copper (determined from the pure $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ -derived monolayer) was subtracted from all copper samples prior to analysis.⁴² Cassie's equation⁴³ (solid lines; bottom graph) relates the surface composition linearly to the wettability of the monolayer by water. Israelachvili and Gee's equation⁴⁴ (dashed line) does not describe the relation between advancing contact angle and surface composition as well as Cassie's equation. The lowest panel includes data obtained from samples that were exposed to the contacting solutions for 2-48 h.



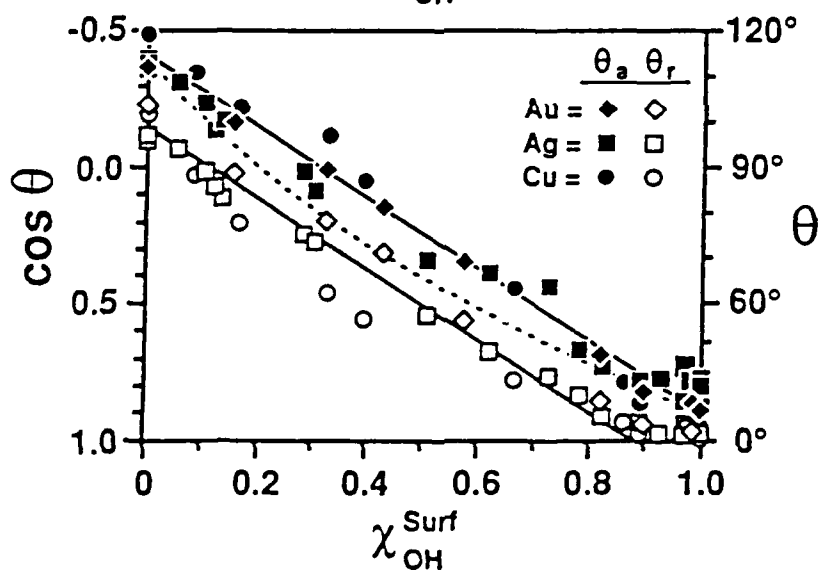
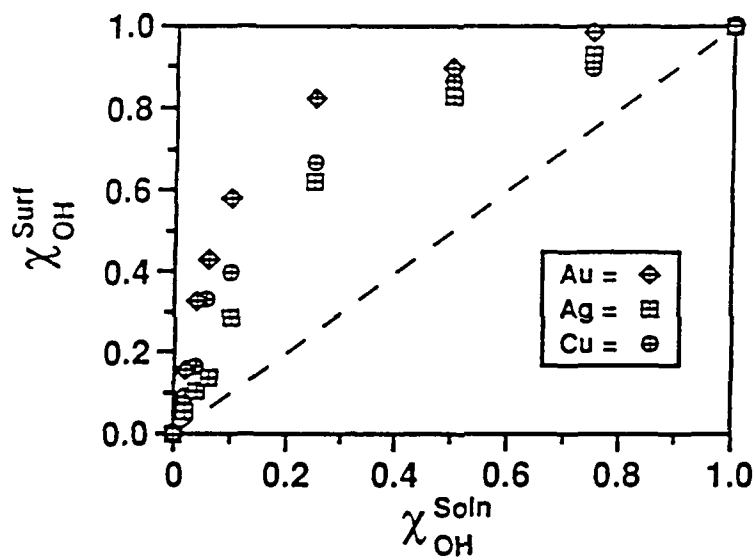
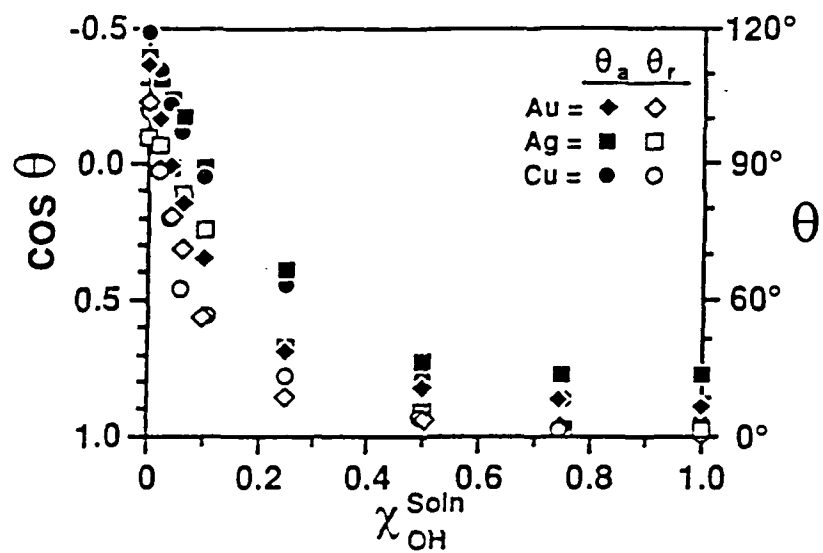
system studied here. We discuss the comparison of these equations further below.

The similarity in surface compositions ($\chi_{\text{OH}}^{\text{Surf}}$) at a common value of solution composition ($\chi_{\text{OH}}^{\text{Soln}}$) is remarkable given the differences in the structures of the monolayers, the strength of the various thiolate-metal bonds, and most importantly, the different chemistries that must be occurring during adsorption of the thiols onto surfaces having differing amounts of oxide. This similarity is particularly striking for silver (which has an oxide surface before exposure to thiol), and gold (which does not).

The hysteresis in the contact angles of water appears constant over all surface compositions (and wettabilities) on each of the three metals. This observation suggests that any islanded domains that may have formed have similar size. The hysteresis on each metal, however, is significantly different ($\text{Cu} > \text{Ag} > \text{Au}$). Since the surface roughness of the metals may be different, hysteresis cannot be related directly to differences in the structures of the monolayers.

Mixed Monolayers Adsorbed from Isooctane Solution. We also examined whether the characteristics of the mixed monolayers on the three metals differed in their response to the solvent used in their preparation. Figure 3 gives data using isooctane as a solvent that parallel those in Figure 2 using ethanol. Bain et al. have shown that the preference of alkanethiols terminated with polar functional groups for a gold surface could be dramatically increased relative to non-polar alkanethiols by using a less polar solvent in adsorption of the SAM.⁹ Figure 3 shows that similar

Figure 3. Comparison of monolayers adsorbed on copper (○), silver (□), and gold (◇) from mixtures of $\text{HS}(\text{CH}_2)_{11}\text{OH}$ and $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ dissolved in isooctane after 1 h exposure. Solutions were 1 mM in total thiol concentration. Data were analyzed and are presented as in Figure 2.



behaviors occur on all three metals using isooctane as the solvent for the alkanethiols, and that all three differ in similar ways from monolayers formed from ethanol. While the $-CH_3$ and $-CH_2OH$ terminated thiols competed about equally for the metal surfaces from ethanol, the latter absorbs preferentially from isooctane. With continued exposure to the contacting solution, χ_{OH}^{surf} increases and the film becomes more hydrophilic. Although the adsorption profiles from isooctane are different from those performed from ethanol, the wetting data are again better described by eq 1 than eq 2 even though the hydrophilicity of the pure hydroxyl surface ($\chi_{CH}^{surf} = 1.0$) is substantially less from isooctane on all three metals than from ethanol. Adsorption of hydroxyl-terminated thiols onto gold from a non-hydrogen-bonding solvent has been shown to result in SAMs that are less hydrophilic than those formed in ethanol.⁹ We do not know the cause of this difference: two possibilities are formation of hydrogen-bonded networks having different structures, or contamination of the polar interface by impurities in solvent.

Ulman⁴⁵ has recently proposed the presence of a wetting transition for SAMs on gold derived for mixtures of $CH_3(CH_2)_{11}SH$ and $HO(CH_2)_{11}SH$. The data in Figures 2 and 3 clearly do not support the presence of a wetting transition for water in these mixed monolayers on gold, silver or copper. No significant departures from Cassie's equation were observed with SAMs adsorbed from ethanol or isooctane on any of the three metals studied here.

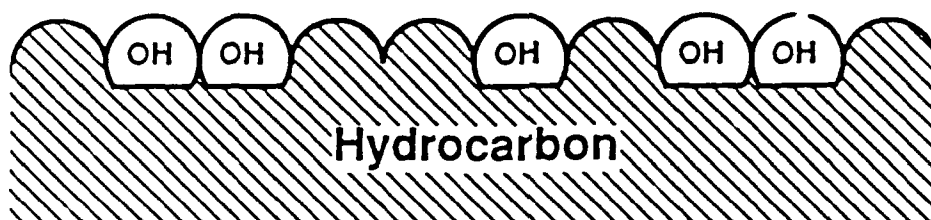
The Relation Between Wettability and Surface

Composition: Cassie vs. Israelachvili-Gee. Israelachvili

and Gee⁴⁴ have suggested eq 2 as an alternative to eq 1 "whenever the size of chemically heterogeneous patches approach molecular or atomic dimensions." We have shown here that SAMs prepared from mixtures of $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ and $\text{HO}(\text{CH}_2)_{11}\text{SH}$ are better described by eq 1 than eq 2. In contrast, Bain et al. have shown that mixed SAMs on gold prepared from $\text{CH}_3(\text{CH}_2)_{10}\text{SH}$ and $\text{HO}(\text{CH}_2)_{11}\text{SH}$ are more hydrophilic than Cassie's relation would suggest.⁹ We have reanalyzed their data and find that the wettability of the mixed monolayers is well described by eq 2.⁴⁶ Why the apparent disagreement in two very similar systems? One possible hypothesis might be that the former system forms SAMs that are highly islanded and the latter does not. While we have no explicit proof concerning the degree of aggregation present in these systems, we feel that the effect can be explained in terms of the differences in the molecular-level heterogeneity present in the two systems, and propose, as one hypothesis, a rationalization based on microscopic roughness.

If one extends Cassie's relation to the molecular level and sums over the surface areas of hydroxyl and methyl groups, a difference between the two systems becomes apparent that may be important. The two systems differ by a single methylene in the methyl-terminated alkanethiol (Figure 4). In the system reported here, the mixed monolayer should, on the average, expose the two functionalities at a common molecular height (Case I). The molecular-level surface area should not change over all surface compositions; the surface area of a hydroxyl should be linearly related to its surface composition. We predict a linear relation

Case I. 1:1 Mixed monolayer derived from
 $\text{HS}(\text{CH}_2)_{11}\text{OH}$ and $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$



Case II. 1:1 Mixed monolayer derived from
 $\text{HS}(\text{CH}_2)_{11}\text{OH}$ and $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$

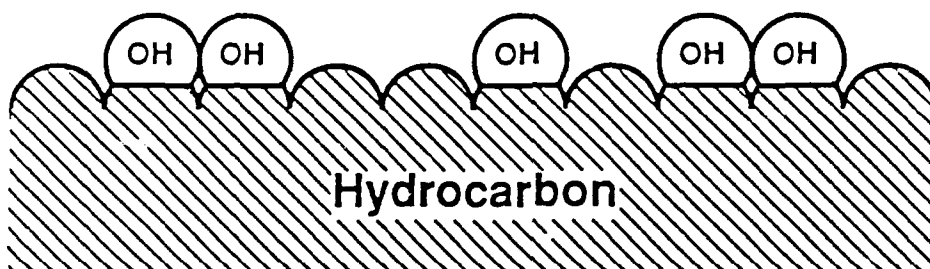


Figure 4. Schematic illustration of the surfaces of monolayers derived from mixtures of $\text{HS}(\text{CH}_2)_{11}\text{OH}$ and $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ (Case I) and $\text{HS}(\text{CH}_2)_{11}\text{OH}$ and $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ (Case II). Cases I and II differ by one methylene in the length of the hydroxyl-terminated chain. Experimentally, the advancing and receding contact angles of water in the two systems are related to the molar fraction of the two components by different expressions: Case I, eq 1; Case II, eq 2. We hypothesize that the difference in wetting may be due to greater exposure of the hydroxyl groups in Case II than in Case I. The diagrams are schematic and oversimplified: both surfaces are disordered to an extent we cannot presently specify.

between wettability and surface composition. In the mixed monolayers studied by Bain et al.,⁵ the hydroxyl groups can, on the average, reside above the plane of the methyl surface (Case II). The surface of the mixed monolayer containing two components of different lengths might be microscopically rougher, and have a larger surface area, than for SAMs derived from either of the two components alone. Because the hydroxyl groups extend above the plane defined by the methyl groups, the fraction of the surface area due to hydroxyl groups should be greater than the surface composition of these groups. Cassie's relation (applied at the molecular level) would predict that the SAMs would appear more hydrophilic than estimated from surface compositions.

Conclusions

ω -Terminated alkanethiols form oriented monolayers on copper, silver and gold surfaces that exhibit similar wetting properties, although they differ significantly in structure (specifically in the contact angles of the trans-extended chains: on gold, 28°; on copper and silver, 13°). In particular, we observed no differences in the wettability of hydroxyl-terminated monolayers. This observation is in disagreement with reports by Ulman et al.²³ The three metals accommodate a variety of tail groups; organic surfaces of a wide range of wettabilities ($\theta_a^{\text{H}_2\text{O}}$ of <15° to ~115°) can be generated on each. Monolayers prepared on each of these metals from mixtures of alkanethiols of similar chain lengths containing different tail groups show similar relations between the compositions of the monolayers and the compositions of the

solutions from which they were formed,⁴⁷ and exhibit similar wettabilities. The wettability of the mixed monolayers derived from alkanethiols having the same number of methylene groups are better described by the relation of Cassie⁴³ than of Israelachvili and Gee.⁴⁴ No wetting transition was observed on SAMs on gold, silver or copper prepared from mixtures of $\text{HS}(\text{CH}_2)_{11}\text{OH}$ and $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$. This observation disagrees with a recent report by Ulman et al.⁴⁵ for SAMs on gold.

Experimental

Materials. 11-Bromo-undecyl t-butyldimethylsilyl ether and most alkanethiols were available from previous studies;^{6,21,48} other materials were obtained from Aldrich and used as received unless specified. Octadecanethiol was distilled under reduced pressure prior to use. 1,1,2,2-Dihydro-perfluorooctyl thiol and 16-mercapto-hexadecanoamide were gifts of Dr. Nandan Rao (Dupont) and Dr. Ralph G. Nuzzo (AT&T Bell Labs), respectively. 16-Cyano-1-hexadecene⁴⁹ and 10-undecenamide⁵⁰ were prepared by literature procedures. Isooctane was percolated through neutral alumina to remove polar products of oxidation. Absolute ethanol (Quantum Chemical Corp.) and isooctane were deoxygenated with bubbling N_2 for 30 min prior to use. Details of the preparation of the following molecules are given in supplementary material to this journal: 11-(2,2,3,3,3-pentafluoropropoxy)-undecanethiol, ethyl-11-mercapto-undecanoate, 11-cyano-1-undecyl thiol, 16-cyano-1-hexadecyl thiol, 21-cyano-1-heneicosyl thiol, 10-mercapto-1-decanol, 22-mercapto-1-docosanol, and 11-mercapto-undecanamide.

Preparation and Characterization of Monolayers.

Procedures were identical with those previously reported;³ substrates were prepared by evaporation in a cryogenically-pumped electron beam evaporator (base pressure = 8×10^{-8} torr). Single-component monolayers were characterized by wetting and XPS after immersion for 12 h in 1 mM deoxygenated ethanolic solutions. Mixed monolayers were formed from deoxygenated solutions that were 1 mM in total thiol concentration; immersion times for mixed monolayers are as stated in the figure captions.

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Supplementary Material Available. Details of the preparation of 11-(2,2,3,3,3-pentafluoropropoxy)-undecanethiol, ethyl-11-mercapto-undecanoate, 11-cyano-1-undecyl thiol, 16-cyano-1-hexadecyl thiol, and 21-cyano-1-heneicosyl thiol, 10-mercapto-1-decanol, 22-mercapto-1-docosanol and 11-mercapto-undecanamide (11 pages). Ordering information is given on any current masthead page.

Footnotes and References

1. This research was supported in part by the Office of Naval Research and by the National Science Foundation (Grant CHE-88-12709). XPS spectra were obtained using instrumental facilities purchased under the DARPA/URI program and maintained by the Harvard University Materials Research Laboratory.
2. Shell Pre-doctoral Fellow 1986-87.
3. Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* submitted.
4. Walczak, M. W.; Chung, C.; Stole, S. M.; Widrig, C. A.; Porter, M. D. *J. Am. Chem. Soc.* 1991, 113, 2370-2378.
5. Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* 1983, 105, 4481-4483. Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* 1987, 107, 2358-2368.
6. Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1989, 111, 321-335.
7. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 5897-5988.
8. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 6560-6561. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 3665-3666. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* 1989, 111, 7164-7175.
9. Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* 1989, 111, 7155-7164.
10. Bain, C. D.; Whitesides, G. M. *Langmuir* 1989, 5, 1370-1378.

11. Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1990, 112, 570-579.
12. For reviews, see Bain, C.D.; Whitesides, G. M. *Angew. Chem. Int. Ed. Engl.* 1989, 101, 522-528 and Whitesides, G. M.; Laibinis, P. E. *Langmuir* 1990, 6, 87-96.
13. Allara, D. L.; Heburd, A. F.; Padden, F. J.; Nuzzo, R. G.; Falcon, D. R. *J. Vac. Sci. Technol. A* 1983, 376-382. Stewart, K. R.; Whitesides, G. M.; Godfried, H. P.; Silvera, I. F. *Rev. Sci. Instrum.* 1986, 57, 1381-1383. Ulman, A.; Tillman, N. *Langmuir* 1989, 5, 1418-1420.
14. Pale-Grosdemange, C.; Simon, E. S.; Prime, K. L.; Whitesides, G. M. *J. Am. Chem. Soc.* 1991, 113, 12-20. Prime, K. L.; Whitesides, G. M. *Science (Washington, DC)* in press.
15. Allen, P. M.; Hill, H. A. O.; Walter, N. J. *J. Electroanal. Chem.* 1984, 178, 69-86. Armstrong, F. A.; Hill, H. A. O.; Walton, N. J. *Acc. Chem. Res.* 1988, 21, 407-413. Tarlov, M. J.; Bowden, E. F. *J. Am. Chem. Soc.* 1991, 113, 1847-1849.
16. Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* 1987, 109, 3559-3558.
17. Chidsey, C. E. D.; Loiacono, D. N. *Langmuir* 1990, 6, 682-691.
18. Non-electroactive *n*-alkanethiols: Li, T., T.-T.; Weaver, M. J. *J. Am. Chem. Soc.* 1984, 106, 6107-6108. Sabatini, E.; Rubinstein, I.; Maoz, R.; Sagiv, J. *J. Electroanal. Chem.* 1987, 219, 365-371. Sabatini, E.; Rubinstein, I. *J. Phys. Chem.* 1987, 91, 6663-6669. Finklea, H. O.; Avery, S.; Lynch, M.; Furttsch, T. *Langmuir* 1987, 3, 409-413. Bunding Lee, K. A.; Mowry, R.;

McLennan, G.; Finklea, H. O. *J. Electroanal. Chem.* 1988, 246, 217-224. Rubinstein, I.; Steinberg, S.; Tor, Y.; Shanzer, A.; Sagiv, J. *Nature* 1988, 332, 426-429. Creager, S. E.; Collard, D. M.; Fox, M. A. *Langmuir* 1990, 6, 1617-1620. Miller, C.; Cuendet, P.; Grätzel, M. *J. Phys. Chem.* 1991, 95, 877-886.

19. Electroactive *n*-alkanethiols: Bunding Lee, K. A. *Langmuir*, 1990, 6, 709-712. Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T. M.; Muijsce, A. M. *J. Am. Chem. Soc.* 1990, 112, 4301-4306. Obeng, Y. S.; Bard, A. J. *Langmuir* 1991, 7, 195-201. Hickman, J. J.; Ofer, D.; Zou, C.; Wrighton, M. S.; Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* 1991, 113, 1128-1132. Chidsey, C. E. D. *Science (Washington, DC)* 1991, 251, 919-922. Hickman, J. J.; Ofer, D.; Laibinis, P. E.; Whitesides, G. M.; Wrighton, M. S. *Science (Washington, DC)* in press. Hickman, J. J.; Laibinis, P. E.; Auerbach, D. I.; Zou, C.; Gardner, T. J.; Whitesides, G. M.; Wrighton, M. S. *Langmuir* submitted.

20. Diem, T.; Czajka, B.; Weber, B.; Regen, S. L. *J. Am. Chem. Soc.* 1986, 108, 6094-6095. Fabianowski, W.; Coyle, L. C.; Weber, B. A.; Granata, R. D.; Castner, D. G.; Sadownik, A.; Regen, S. L. *Langmuir* 1989, 5, 35-41.

21. Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* 1990, 112, 558-569.

22. Sum-frequency vibrational spectroscopy: Harris, A. L.; Chidsey, C. E. D.; Levinos, N. J.; Loiacono, D. N. *Chem. Phys. Lett.* 1987, 141, 350-356. TEM: Strong, L.; Whitesides, G. M. *Langmuir*, 1988, 4, 546-558; see ref 17 for a reanalysis of part of the data in this paper. Helium diffraction: Chidsey, C. E. D.;

Liu, G.-Y.; Rowntree, P.; Scoles, G. *J. Chem. Phys.* 1989, 91, 4421-4423. Camillone III, N.; Chidsey, C. E. D.; Liu, G.-Y.; Putvinski, T. M.; Scoles, G. *J. Chem. Phys.* submitted. IR spectroscopy: Nuzzo, R. G.; Korenic, E. M.; Dubois, L. H. *J. Chem. Phys.* 1990, 93, 767-773.

23. Tillman, N.; Ulman, A.; Penner, T. L. *Langmuir* 1989, 5, 101-111. Ulman, A.; Eilers, J. E. *Angew. Chem.* submitted.

24. Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. *J. Colloid Sci.* 1946, 1, 513-538. Shafrin, E. G.; Zisman, W. A. *J. Colloid Sci.* 1952, 7, 166-177. Sagiv, J. *J. Am. Chem. Soc.* 1980, 102, 92-98. Maoz, R.; Sagiv, J. *J. Colloid Interface Sci.* 1984, 100, 465-496. Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir*, 1988, 4, 365-385.

25. Schulman, F.; Zisman, W. A. *J. Colloid Sci.* 1952, 7, 465-481. Bigelow, W. C.; Brockway, L. O. *J. Colloid Sci.* 1956, 11, 60-68. Allara, D.L.; Nuzzo, R.G. *Langmuir* 1985, 1, 45-52. Schlotter, N. E.; Porter, M. D.; Bright, T. B.; Allara, D. L. *Chem. Phys. Lett.* 1986, 132, 93-98.

26. Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir*, 1989, 5, 1074-1087.

27. Netzer, L.; Sagiv, J. *J. Am. Chem. Soc.* 1983, 105, 674-676. Netzer, L.; Iscovici, R.; Sagiv, J. *Thin Solid Films* 1983, 99, 235-241. Netzer, L.; Iscovici, R.; Sagiv, J. *Thin Solid Films* 1983, 100, 67-76. Tillman, N.; Ulman, A.; Penner, T. L. *Langmuir*, 1989, 5, 101-111.

28. Tillman, N.; Ulman, A.; Elman, J. F. *Langmuir*, 1989, 5, 1020-1026.

29. Tillman, N.; Ulman, A.; Schildkraut, J. S.; Penner, T.L.
J. Am. Chem. Soc. 1988, 110, 6136-6144.

30. The wettabilities of the alcohol and carboxylic acid surfaces generated by chemical transformation of less polar terminal groups on alkylsiloxane monolayers ($\theta_a^{H_2O} \approx 30-55^\circ$)^{26,27} are significantly less than that found on surfaces formed on gold from the corresponding ω -terminated alkanethiols or disulfides ($\theta_a^{H_2O} < 15^\circ$).^{6,10,21}

31. Pearson, R. G. *J. Am. Chem. Soc.* 1963, 85, 3533-3539.
Huheey, J. E. *Inorganic Chemistry*; Harper & Row: New York, 1978; pp 276-280.

32. For an example of the degree of discrimination possible between hard ($-\text{CO}_2\text{H}$) and soft ($-\text{SH}$) adsorbates for hard (Al_2O_3) and soft (Au) surfaces, see Laibinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Whitesides, G. M. *Science (Washington, DC)* 1989, 245, 845-847.

33. Ethanol was chosen as the contacting solvent due to its low cost and toxicity, and its previous use to generate alkanethiolate surfaces on gold of a wide range of wettabilities.^{5-10,21} Less polar solvents yield ω -hydroxy-alkanethiolate monolayers on gold of decreased hydrophilicity.⁹

34. Allara, D. L.; Atre, S. V.; Ellinger, C. A.; Snyder, R. G.
J. Am. Chem. Soc. 1991, 113, 1852-1854.

35. Wilson, M. D.; Ferguson, G. S.; Whitesides, G. M. *J. Am. Chem. Soc.* 1990, 112, 1244-1245.

36. The intensity of the photoelectron peak due to an underlayer decreases exponentially with the thickness of the

overlayer due to inelastic scattering of photoelectrons from the underlayer with the overlayer (Briggs, D.; Seah, M. *Practical Surface Analysis*; Wiley: Chichester, 1983; p 211).

37. IR could also be used to characterize the structure of these monolayers though absolute determination of structure by IR is confounded by choice of a reference state. We believe that once a standard (*n*-alkanethiols) has been evaluated;^{3,4,16,21} comparison to it by XPS is not only more convenient but is probably also no less accurate or precise. The thickness of the SAM can be estimated from the attenuation of photoelectrons by the film.³⁶ Assuming the SAM to contain trans-extended polymethylene chains, the thickness is related to the angle the adsorbate is oriented on the metal. Details pertaining to head group orientation and twisting of the polymethylene chains are, however, determinable by IR and not by XPS.

38. Seah, M. P.; Dench, W. A. *Surf. Interface Anal.* 1979, 1, 2-11.

39. Nuzzo et al.²¹ have shown by IR that ω -substituted-pentadecanethiolate monolayers on gold have similar structures when the head group is commensurate in size with the polymethylene chain.

40. Hautman, J.; Klein, M. L. *J. Chem. Phys.* 1989, 91, 4994-5001.

41. At room temperature, it is difficult to imagine that the tail groups would adopt a single orientation. The structure of alkanethiolate monolayers on gold (by helium diffraction and IR,

respectively) is more crystalline at low temperatures (~100 K) than at room temperature.²²

42. The different O(1s) peaks overlapped slightly (binding energy, peak width: oxide = 530.4 eV, ~2.0 eV; hydroxyl = 533.0 eV, ~2.0 eV) but could be resolved via chi square analysis of the composite signal.

43. Cassie, A. B. D. *Discuss. Faraday Soc.* 1948, 3, 11-16.

44. Israelachvili, J. N.; Gee, M. L. *Langmuir* 1989, 5, 288-289.

45. Ulman, A.; Evans, S. D.; Shnidman, Y.; Sharma, R.; Eilers, J. E.; Chang, J. C. *J. Am. Chem. Soc.* 1991, 113, 1499-1506.

46. Bain et al.⁹ assumed a linear relationship between f_{OH} and χ_{OH}^{surf} which may not be applicable to monolayers derived from mixtures of HS(CH₂)₁₁OH and HS(CH₂)₁₀CH₃ (see text). The wettability of these mixed monolayers can be related to χ_{OH}^{surf} by eq 2 if one assumes $\chi_{OH}^{surf} = f_{OH}$.

47. When the two alkanethiols differ in chain length (C₁₁ and C₂₂), the surface compositions of monolayers formed on silver and gold from solutions containing mixtures of the two thiols can differ by up to ~40 % (Laibinis, P. E.; Fox, M. A.; Folkers, J. P.; Whitesides, G. M. Manuscript in preparation).

48. Laibinis, P. E.; Janes, L. E.; Prime, K. L.; Nuzzo, R. G.; Whitesides, G. M. Manuscript in preparation.

49. Balanchander, N.; Sukenik, C. *Langmuir* 1990, 6, 1621-1627.

50. Aschan, O. *Chem. Ber.* 1898, 31, 2344-2350. Dobashi, Y.; Hara, S. *J. Org. Chem.* 1987, 52, 2490-2496.

Figure Captions

Figure 1. Intensity of photoelectrons due to the underlying metal substrate for various monolayers adsorbed on the surfaces of copper (\square), silver (\diamond), and gold (\circ) from absolute ethanol. We define "molecular length" as the number of contiguous atoms in the adsorbate spanning the monolayer. (For example, for metal/SCH₂CO₂CH₃ the molecular length would be 6.) The numeric labels refer to compounds listed in Table I. Absolute photoelectron intensities are a function of instrumental parameters and the sets of data have been offset vertically to facilitate comparison; only the slopes are important here. The kinetic energies of photoelectrons for each graph are similar: Au(4f_{7/2}) = 1402 eV and Cu(3p) = 1412 eV; Au(4d) = 1143 eV and Ag(3d_{5/2}) = 1119 eV. The filled symbols correspond to SAMs derived from *n*-alkanethiols (X = CH₃). Dashed lines were determined from linear least square fits to data obtained from adsorption of *n*-alkanethiols on the three metals; the higher slopes obtained on copper and silver demonstrate that the SAMs formed on these metals are oriented closer to the surface normal than those formed on gold: Au(4d) = -0.049 vs. Ag(3d_{5/2}) = -0.057; Au(4f_{7/2}) = -0.041 vs. Cu(3p) = -0.051.

Figure 2. Comparison of monolayers adsorbed on copper (\circ), silver (\square), and gold (\diamond) from mixtures of HS(CH₂)₁₁OH and HS(CH₂)₁₁CH₃ dissolved in ethanol after 2 h exposure. Solutions were 1 mM in total thiol concentration. Advancing and receding

contact angles (filled and open symbols, respectively) were measured on static drops of water. Surface compositions (patterned symbols) were determined from XPS by scaling the O(1s) signal to that obtained on the pure $\text{HS}(\text{CH}_2)_{11}\text{OH}$ -derived monolayer; the background level of oxygen on copper (determined from the pure $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ -derived monolayer) was subtracted from all copper samples prior to analysis.⁴² Cassie's equation⁴³ (solid lines; bottom graph) relates the surface composition linearly to the wettability of the monolayer by water. Israelachvili and Gee's equation⁴⁴ (dashed line) does not describe the relation between advancing contact angle and surface composition as well as Cassie's equation. The lowest panel includes data obtained from samples that were exposed to the contacting solutions for 2-48 h.

Figure 3. Comparison of monolayers adsorbed on copper (○), silver (□), and gold (◇) from mixtures of $\text{HS}(\text{CH}_2)_{11}\text{OH}$ and $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ dissolved in isooctane after 1 h exposure. Solutions were 1 mM in total thiol concentration. Data were analyzed and are presented as in Figure 2.

Figure 4. Schematic illustration of the surfaces of monolayers derived from mixtures of $\text{HS}(\text{CH}_2)_{11}\text{OH}$ and $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ (Case I) and $\text{HS}(\text{CH}_2)_{11}\text{OH}$ and $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ (Case II). Cases I and II differ by one methylene in the length of the hydroxyl-terminated chain. Experimentally, the advancing and receding contact angles of water in the two systems are related to the molar fraction of the two components by different expressions: Case I, eq 1; Case II, eq 2.

We hypothesize that the difference in wetting may be due to greater exposure of the hydroxyl groups in Case II than in Case I. The diagrams are schematic and oversimplified: both surfaces are disordered to an extent we cannot presently specify.

SUPPLEMENTARY MATERIAL

ω -Terminated Alkanethiolate Monolayers on Surfaces of
Copper, Silver and Gold Have Similar Wettabilities.

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Materials. All materials were obtained from Aldrich and used as received unless specified below. Thioacetic acid was obtained from Fluka. 11-Bromo-undecene was obtained from Pfaltz & Bauer, NaCN from Fisher, 9-decenol from Alfa, and K_2CO_3 from Sigma. Photolyses were conducted with a 100 W medium pressure Hg lamp. Column chromatographic purifications were performed with 230-400 mesh silica gel (EM Science). Melting points are reported uncorrected. Elemental analyses were performed by Oneida Research Services.

11-(2,2,3,3,3-Pentafluoropropoxy)-undecanethiol (2). Sodium (0.50 g, 22 mmol) was added to a solution of 2,2,3,3,3-pentafluoro-propanol (3.55 g, 23.7 mmol) in 30 mL dist THF and stirred under N_2 for 1 h. A solution of 11-bromo-1-undecene (3.50 g, 15.0 mmol) in 40 mL dist THF was added and the mixture refluxed for 72 h. The reaction was quenched by addition of 30 mL dist H_2O and subsequently extracted with CH_2Cl_2 (3 x 25 mL). The organic extracts were combined and concentrated. 11-(2,2,3,3,3-pentafluoropropoxy)-1-undecene was separated from remaining 11-bromo-1-undecene by chromatography (5% EtOAc/hexanes) and obtained as a colorless liquid (3.02 g, 10.0 mmol, 66%). 1H NMR ($CDCl_3$, 250 MHz) δ 5.80 (m, 1 H), 4.95 (m, 1 H), 4.93 (m, 1 H), 3.85 (t, J = 13 Hz, 2 H), 3.56 (t, J = 7 Hz, 2 H), 2.02 (quart, J = 6 Hz, 2 H), 1.55 (m, 4 H), 1.2-1.3 (m, 10 H).

A solution of 11-(2,2,3,3,3-pentafluoropropoxy)-1-undecene (2.96 g, 9.8 mmol), 4 mL of thioacetic acid, and ~10 mg of AIBN were combined in 40 mL of THF and photolyzed for 6 h.¹ The solution was added to 200 mL of dist H_2O and extracted with Et_2O (3 x 50 mL).

The organic extracts were combined, dried over MgSO_4 and concentrated to give a yellow oil which was purified by chromatography (5% EtOAc/hexanes) and gave 11-(2,2,3,3,3-pentafluoropropoxy)-1-undecyl thioacetate as a colorless liquid (2.85 g, 7.5 mmol, 77%). ^1H NMR (CDCl_3 , 300 MHz) δ 3.85 (t, J = 13 Hz, 2H), 3.56 (t, J = 7 Hz, 2 H), 2.84 (t, J = 7 Hz, 2 H), 2.30 (s, 3 H), 1.55 (m, 4 H), 1.31 (t, J = 7 Hz, 1 H), 1.2-1.3 (m, 10 H).

A solution of 11-(2,2,3,3,3-pentafluoropropoxy)-1-undecyl thioacetate (2.74 g, 7.24 mmol) in 30 mL MeOH was deoxygenated with N_2 for 30 min. Granular K_2CO_3 (0.25 g, Sigma) was added and the mixture stirred for 2 h under N_2 . The reaction was quenched by addition of 10% aqueous HCl and the title compound separated by extraction with Et₂O (3 x 25 mL). The organic extracts were combined, dried with MgSO_4 , and concentrated. The oil was purified by chromatography (5% EtOAc/hexanes) and the title compound was obtained as a colorless liquid (1.87 g, 5.56 mmol, 77%). ^1H NMR (CDCl_3 , 300 MHz) δ 3.85 (t, J = 13 Hz, 2 H), 3.56 (t, J = 7 Hz, 2 H), 2.50 (quart, J = 7 Hz, 2 H), 1.5-1.6 (m, 4 H), 1.31 (t, J = 7 Hz, 1 H), 1.2-1.3 (m, 10 H). Anal. Calcd (Found) for $\text{C}_{14}\text{H}_{25}\text{F}_5\text{OS}$: C, 49.99 (50.29); H, 7.49 (7.44); S, 9.53 (9.69).

Ethyl-11-mercapto-undecanoate (9). Ethyl undecenoate (10.6 g, 50.0 mmol), thiolacetic acid (5 mL) and ~5 mg AIBN were combined in 40 mL of THF and photolyzed¹ for 12 h and subsequently concentrated to give a yellow oil. The oil was dissolved in 60 mL abs EtOH and the solution deoxygenated with bubbling N_2 for 30 min. Conc HCl (5 mL) was added and the solution was refluxed for 4 h

under N_2 . After concentration, the title compound was obtained by vacuum distillation (120-123 $^{\circ}C$, <1 torr) as a colorless liquid (7.70 g, 31.3 mmol, 62%). 1H NMR ($CDCl_3$, 300 MHz) δ 4.10 (quart, J = 7 Hz, 2 H), 2.50 (quart, J = 7 Hz, 2 H), 2.26 (t, J = 7 Hz, 2 H), 1.58 (m, 4 H), 1.30 (t, J = 7 Hz, 1 H), 1.2-1.3 (m, 12 H), 1.23 (t, J = 7 Hz, 3 H). Anal. Calcd (Found) for $C_{13}H_{26}O_2S$: C, 63.37 (63.33); H, 10.64 (10.68); S, 13.01 (13.82).

11-Cyano-1-undecyl thiol (12). A solution of 11-bromo-1-undecene (3.90 g, 16.7 mmol) and NaCN (1.53 g, 31.2 mmol) in 30 mL DMSO were stirred for 4 d.² The solution was combined with 50 mL dist H_2O and extracted with Et_2O (3 x 25 mL). The organic extracts were concentrated to give 11-cyano-1-undecene (2.83 g, 15.8 mmol, 94%) as a colorless oil which was not purified further. 1H NMR ($CDCl_3$, 250 MHz) δ 5.7-5.9 (m, 1 H), 4.95 (m, 1 H), 4.94 (m, 1 H), 2.31 (t, 2 H, J = 7 Hz), 2.02 (quart, 2 H, J = 7 Hz), 1.64 (m, 2 H), 1.2-1.5 (m, 12 H).

A solution of 11-cyano-1-undecene (2.83 g, 15.8 mmol), thiolacetic acid (3 mL), AIBN (5 mg), and 50 mL MeOH were photolyzed for 12 h.¹ The solution was concentrated and 11-cyano-1-undecyl thioacetate (3.42 g, 13.4 mmol, 85%) obtained by chromatography (10% EtOAc/hexanes) as a colorless liquid. 1H NMR ($CDCl_3$, 300 MHz) δ 2.87 (t, 2 H, J = 7 Hz), 2.34 (t, 2 H, J = 7 Hz), 2.32 (s, 3 H), 1.65 (quint, 2 H, J = 7 Hz), 1.55 (m, 2 H), 1.2-1.5 (m, 14 H).

A solution of 11-cyano-1-undecyl thioacetate (1.20 g, 4.70 mmol) in 15 mL MeOH was deoxygenated with N_2 for 30 min. Granular K_2CO_3 (0.5 g) was added and the mixture was stirred for 3 h under N_2 .

The reaction mixture was quenched with 10% HCl and extracted with Et₂O (3 x 20 mL). The organic extracts were combined and concentrated. Chromatography (10% EtOAc/hexanes) afforded 11-cyano-undecyl thiol (480 mg, 2.25 mmol, 48%) and di(11-cyano-undecyl) disulfide (300 mg, 0.71 mmol, 30%) as a colorless liquid and a white solid, respectively. 11-Cyano-undecyl thiol (12). ¹H NMR (CDCl₃, 300 MHz) δ 2.50 (quart, 2 H, J = 7 Hz), 2.31 (t, 2 H, J = 7 Hz), 1.63 (m, 4 H), 1.31 (t, 1 H, J = 7 Hz), 1.2-1.4 (m, 14 H). Anal. Calcd (Found) for C₁₂H₂₃NS: C, 67.55 (67.69); H, 10.86 (11.00); N, 6.56 (6.41); S, 15.02 (14.70). Di(11-cyano-undecyl) disulfide. M.P. 32-33 °C. ¹H NMR (CDCl₃, 300 MHz) δ 2.65 (t, 4 H, J = 7 Hz), 2.31 (t, 4 H, J = 7 Hz), 1.63 (m, 8 H), 1.2-1.45 (m, 28 H). Anal. Calcd (Found) for C₂₄H₄₄N₂S₂: C, 67.87 (67.89); H, 10.44 (10.55); N, 6.60 (6.45); S, 15.10 (14.69).

16-cyano-1-hexadecyl thiol (13). A solution of 16-cyano-1-hexadecene³ (1.21 g, 4.87 mmol), thiolacetic acid (2 g), AIBN (10 mg) and 40 mL THF was photolyzed for 8 h.¹ The solution was concentrated to yield a yellow solid which was purified by chromatography (10% EtOAc/hexanes) to yield 16-cyano-1-hexadecyl thioacetate as a white solid (1.45 g, 4.46 mmol, 92%). M.P. 56-57 °C. ¹H NMR (CDCl₃, 250 MHz) δ 2.84 (t, 2 H, J = 7 Hz), 2.32 (t, 2 H, J = 7 Hz), 2.30 (s, 3 H), 1.64 (quint, 2 H, J = 7 Hz), 1.51 (m, 2 H), 1.2-1.5 (m, 24 H). Anal. Calcd (Found) for C₁₉H₃₅NOS: C, 70.10 (70.23); H, 10.84 (11.26); N, 4.30 (4.22); S, 9.85 (10.03).

A solution of 16-cyano-1-hexadecyl thioacetate in 50 mL MeOH was deoxygenated with N₂ for 20 min prior to addition of granular K₂CO₃ (1.25 g) and subsequent stirring under N₂ for 2 h. The reaction

was quenched by addition of 3 mL conc HCl and 50 mL dist H₂O, and extracted with Et₂O (3 x 20 mL). The organic extracts were combined and concentrated to yield a white solid that contained two primary materials. Separation by chromatography (10% EtOAc/hexanes) afforded 16-cyano-1-hexadecyl thiol (1.09 g, 3.85 mmol, 90%) and di(16-cyano-hexadecyl) disulfide (0.12 g, 0.21 mmol, 10%) as white solids. **16-Cyano-hexadecyl thiol (13).** M.P. 39.5-40 °C. ¹H NMR (CDCl₃, 300 MHz) δ 2.50 (quart, 2 H, J = 7 Hz), 2.31 (t, 2 H, J = 7 Hz), 1.61 (m, 4 H, J = 7 Hz), 1.30 (t, 1 H, J = 7 Hz), 1.2-1.5 (m, 24 H). Anal. Calcd (Found) for C₁₇H₃₃NS: C, 72.02 (72.03); H, 11.73 (11.93); N, 4.94 (4.82); S, 11.31 (12.34). **Di-(16-cyano-hexadecyl) disulfide.** M.P. 61-64 °C. ¹H NMR (CDCl₃, 300 MHz) δ 2.66 (t, 4 H, J = 7 Hz), 2.32 (t, 4 H, J = 7 Hz), 1.65 (m, 4 H), 1.2-1.5 (m, 52 H). Anal. Calcd (Found) for C₃₄H₆₄N₂S₂: C, 72.28 (72.50); H, 11.42 (11.76); N, 4.96 (4.94); S, 11.35 (11.76).

21-cyano-1-heneicosyl thiol (14). A solution of 21-bromo-1-heneicosene (974 mg, 2.61 mmol) and NaCN (170 mg, 3.5 mmol) in 15 mL DMSO were stirred at 80 °C for 1 h.² After cooling to R.T., the solution was combined with 35 mL dist H₂O and extracted with hexanes (3 x 20 mL). The organic extracts were combined and concentrated to yield a white solid which was purified by chromatography (20% EtOAc/hexanes) to yield 21-cyano-1-heneicosene as a white solid (784 mg, 2.45 mmol, 94%). M.P. 44-45.5 °C. ¹H NMR (CDCl₃, 250 MHz) δ 5.80 (m, 1 H), 4.95 (m, 1 H), 4.93 (m, 1 H), 2.31 (t, J = 7 Hz), 2.01 (quart, J = 7 Hz), 2 H), 1.64 (quint, J = 7 Hz, 2 H), 1.2-1.4 (m, 34 H).

A solution of 21-cyano-1-heneicosene (760 mg, 2.38 mmol), thiolacetic acid (2 g), AIBN (10 mg) and 40 mL THF was photolyzed for 2 h.¹ The solution was combined with 40 mL dist H₂O and extracted with Et₂O (3 x 20 mL). The organic extracts were combined and concentrated to give a solid that was purified by chromatography (25% EtOAc/hexanes) to yield 21-cyano-1-heneicosyl thioacetate as a white solid (765 mg, 1.93 mmol, 81%). M.P. 65-66 °C. ¹H NMR (CDCl₃, 300 MHz) δ 2.84 (t, 2 H, J = 7 Hz), 2.30 (t, 2 H, J = 7 Hz), 2.29 (s, 3 H), 1.61 (m, 2 H), 1.2-1.5 (m, 36 H).

A solution of 21-cyano-1-heneicosyl thioacetate in 40 mL MeOH was deoxygenated with N₂. Granular K₂CO₃ (0.5 g) was added and the mixture was stirred for 2 h under N₂. The reaction was quenched by addition of 5 mL conc HCl, added to 50 mL dist H₂O and extracted with Et₂O (3 x 25 mL). The organic extracts were combined and concentrated. Purification by chromatography (1:8 EtOAc/hexanes) yielded the title compound as a white solid (451 mg, 1.28 mmol, 69%). M.P. 47-48 °C. ¹H NMR (CDCl₃, 300 MHz) δ 2.50 (quart, 2 H, J = 7 Hz), 2.31 (t, 2 H, J = 7 Hz), 1.61 (m, 4 H, J = 7 Hz), 1.30 (t, 1 H, J = 7 Hz), 1.2-1.5 (m, 34 H). Anal. Calcd (Found) for C₂₂H₄₃NS: C, 74.72 (75.18); H, 12.26 (12.33); N, 3.96 (3.89); S, 9.07 (8.70).

10-Mercapto-1-decanol (17). A solution of 9-decenol (3.21 g, 20.6 mmol), thioacetic acid (2 mL) and AIBN (5 mg) in THF (50 mL) was photolyzed for 12 h.¹ The solution was concentrated, and 10-thioacetyl-1-decanol was obtained by chromatography (15% EtOAc/hexanes) and further purified by recrystallization from hexanes (3.75 g, 16.1 mmol, 79%). M.P. 28.5-29.3 °C. ¹H NMR

(CDCl₃, 250 MHz) δ 3.61 (t, 2 H, J = 7 Hz), 2.83 (t, 2 H, J = 7 Hz), 2.29 (s, 3 H), 1.53 (m, 4 H), 1.2-1.4 (m, 12 H). Anal. Calcd (Found) for C₁₂H₂₄O₂S: C, 62.02 (62.31); H, 10.41 (10.76); S 13.80 (13.34).

A methanolic solution (50 mL) of 10-thioacetyl-1-decanol (1.43 g, 6.17 mmol) was deoxygenated with bubbling N₂ for 30 min. Granular K₂CO₃ (0.5 g) was added and the mixture stirred for 2 h under N₂. The reaction was quenched with glacial AcOH (2 mL) and added to 50 mL dist H₂O. Extraction with CHCl₃ (3 x 25 mL) and purification by chromatography (20% EtOAc/hexanes) gave the title compound as a colorless oil (1.05 g, 5.53 mmol, 90 %). ¹H NMR (CDCl₃, 300 MHz) δ 3.62 (t, 2 H, J = 7 Hz), 2.50 (quart, 2 H, J = 7 Hz), 1.45-1.6 (m, 4 H), 1.31 (t, 1 H, J = 7 Hz), 1.2-1.4 (m, 12 H).

21-Docosenyl t-butyldimethylsilyl ether. A solution of 10-undecylenic magnesium bromide was prepared by dropwise addition of 11-bromo-1-undecene (5.59 g, 24.0 mmol) in 20 mL THF into a flame-dried flask containing Mg and 50 mL THF. The Grignard solution was then added dropwise to a flask containing 11-bromo-undecyl t-butyldimethylsilyl ether⁴ (4.53 g, 12.4 mmol), and Li₂CuCl₄ (0.3 mmol) in 50 mL THF at 0 °C.⁵ The reaction warmed to room temperature overnight. The reaction mixture was added to an aqueous solution of NH₄Cl (30 g in 125 mL dist H₂O) to remove the copper salts. The layers were separated and the aqueous fraction extracted with 50 mL THF. The organic extracts were combined and concentrated to give a yellow oil. The title compound was obtained by chromatography (hexanes followed by 2% EtOAc/hexanes)

as a colorless oil (3.92 g, 8.94 mmol, 72%). ^1H NMR (CDCl_3 , 250 MHz) δ 5.80 (m, 1 H), 4.95 (d, 1 H, $J = 28$ Hz), 4.93 (m, 1 H), 3.57 (t, 2 H, $J = 7$ Hz), 2.02 (quart, 2 H, $J = 7$ Hz), 1.49 (m, 2 H, $J = 7$ Hz), 1.2-1.4 (m, 34 H), 0.87 (s, 6 H), 0.03 (s, 9 H).

21-Docosen-1-ol. A solution of tetrabutylammonium fluoride in THF (20 mL, 1.0 M) was added to 21-docosenyl t-butyldimethylsilyl ether (3.92 g, 8.94 mmol) in 40 mL THF. The reaction was stirred for 2.5 h and concentrated under reduced pressure. The title compound was obtained by chromatography (1:4 EtOAc/hexanes) as a white solid (2.70 g, 8.32 mmol, 93%). M.P. 60-61°C. ^1H NMR (CDCl_3 , 300 MHz) δ 5.79 (m, 1 H), 4.95 (d, 1 H, $J = 32$ Hz), 4.93 (m, 1 H), 3.61 (t, 2 H, $J = 7$ Hz), 2.01 (quart, 2 H, $J = 7$ Hz), 1.54 (m, 2 H, $J = 7$ Hz), 1.2-1.4 (m, 34 H).

22-Mercapto-1-Docosanol (20). A solution of 21-docosen-1-ol (2.01 g, 6.21 mmol), thioacetic acid (2 mL), AIBN (2 mg) and THF (50 mL) was photolyzed for 4 h. The reaction mixture was added to 40 mL dist H_2O and extracted with Et_2O (2 x 25 mL). The organic extracts were combined and concentrated to give a white solid. The material was dissolved in MeOH (100 mL) and the solution purge with N_2 for 30 min. Conc HCl (10 mL) was added and the solution refluxed for 4 h. Upon cooling, the product crystallized out and was collected by filtration. The title compound was purified further by recrystallization from hexanes (1.27 g, 3.55 mmol, 57%). M.P. 72-73 °C. ^1H NMR (CDCl_3 , 250 MHz) δ 3.62 (t, 2 H, $J = 7$ Hz), 2.50 (quart, 2 H, $J = 7$ Hz), 1.45-1.65 (m, 4 H), 1.31 (t, 1 H, $J = 7$ Hz), 1.2-1.4 (m, 36 H). Anal. Calcd. (Found) for $\text{C}_{22}\text{H}_{46}\text{OS}$: C 73.67 (73.89); H 12.93 (12.83).

11-Mercapto-undecanamide (21). A solution of 10-undecanamide⁶ (3.04 g, 16.6 mmol), thioacetic acid (3 mL), AIBN (5 mg), in 80 mL THF/MeOH (1:1) was photolyzed for 12 h.² The reaction mixture was concentrated and gave a solid. Recrystallization from EtOH/H₂O gave 11-thioacetyl-undecanamide as a white solid (3.64 g, 14.0 mmol, 85%). M.P. 91-92 °C. ¹H NMR (CDCl₃, 300 MHz) δ 5.42 (br, 2 H), 2.83 (t, 2 H, *J* = 7 Hz), 2.29 (s, 3 H), 2.19 (t, 2 H, *J* = 7 Hz), 1.60 (m, 2 H, *J* = 7 Hz), 1.53 (m, 2 H, *J* = 7 Hz), 1.2-1.4 (m, 12 H). Anal. Calcd (Found) for C₁₃H₂₅NO₂S: C, 60.19 (59.85); H, 9.71 (9.90); N, 5.40 (5.45).

A methanolic solution (40 mL) of 11-thioacetyl-undecanamide (1.06 g, 4.10 mmol) was deoxygenated with N₂ for 30 min. Granular K₂CO₃ (0.3 g) was added and the mixture stirred under N₂ for 12 h. The reaction was quenched by addition of 3 mL glacial acetic acid and added to 50 mL dist H₂O. The title compound was obtained by extraction with CHCl₃ (3 x 30 mL) and subsequent concentration. Purification by column chromatography (1% MeOH/CHCl₃) gave 11-mercapto-undecanamide as a white solid (0.50 g, 2.3 mmol, 56%). M.P. 90-91 °C. ¹H NMR (CDCl₃, 300 MHz) δ 5.57 (br, 2 H), 2.49 (quart, 2 H, *J* = 7 Hz), 2.20 (t, 2 H, *J* = 7 Hz), 1.45-1.6 (m, 4 H), 1.30 (t, 1 H, *J* = 7 Hz), 1.2-1.4 (m, 12 H). Anal. Calcd (Found) for C₁₁H₂₃NOS: C, 60.78 (61.01); H, 10.67 (11.01); N, 6.44 (6.36); S, 14.75 (14.60).

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References

1. Janssen, M. J. in *The Chemistry of Carboxylic Acids and Esters*; Patai, S., Ed.; Interscience: New York, 1969; pp 720-723.
Griesbaum, K. *Angew. Chem. Int. Ed. Engl.* 1970, 9, 273-287.
2. Friedman, L.; Schechter, H. *J. Org Chem.* 1960, 25, 877-879.
3. Balanchander, N.; Sukenik, C. *Langmuir* 1990, 6, 1621-1627.
4. Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1989, 111, 321-335.
5. Tamura, M.; Kochi, J. *Synthesis* 1971, 303-305.
6. Aschan, O. *Chem. Ber.* 1898, 31, 2344-2350. Dobashi, Y.; Hara, S. *J. Org. Chem.* 1987, 52, 2490-2496.

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